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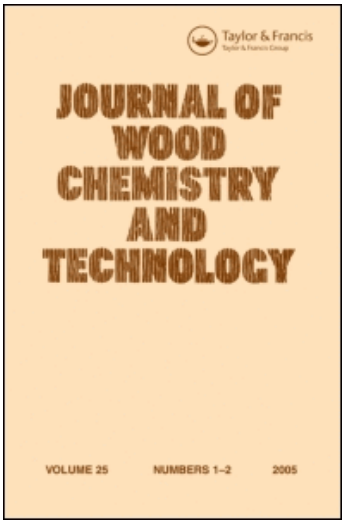

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Measuring Retention of Chromated Copper Arsenate in Conifer Sapwood by Direct-Scan X-Ray Techniques

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MEASURING RETENTION OF CHROMATED COPPER ARSENATE IN CONIFER SAPWOOD BY DIRECT-SCAN X-RAY TECHNIQUES

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ABSTRACT

This study was designed to indicate how well direct-scan X-raying predicts preservative retention and distribution of chromated copper arsenate (CCA) in wafers of conifer sapwood. The intensity of X-rays passed through western hemlock wafers treated with varying concentrations of CCA solutions was inversely proportional to preservative concentration. X-ray intensities predicted 98% of the variation in preservative retention among the wafers. Intensity of direct-scan X-rays passed through selected test materials was consistent over a 9-month span. X-ray intensity over 1000 readings at a single scan point had a coefficient of variation of 0.1%. The strong relationship between direct-scan X-ray intensity and preservative retention, as well as the repeatability of intensity readings over time and the small variation in intensity readings at each data point, indicate that direct-scan X-ray techniques can be used to assess preservative retention and distribution in wood treated with inorganic arsenicals such as CCA.

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INTRODUCTION

Inorganic arsenicals such as chromated copper arsenate are increasingly used to protect wood from decay. Wood treated with these chemicals now represents over 60% of the total annual volume of treated wood[1]. Quality standards are maintained by regularly removing samples and determining their chemical content by such analytical techniques as X-ray fluorescence or atomic absorption spectroscopy.[2] While these techniques are reliable, they generally require relatively large quantities of wood per specimen (~1 g), and the resulting analysis represents the average chemical content of the specimen. Averages are sufficient for quality control procedures; however, they are not adequate for determining the spatial distribution of a chemical in the wood. Analyses of small specimens by more sophisticated methods such as ion-coupled plasma atomic absorption spectroscopy can improve precision, but such methods also require blending of wood material. Ideally, spatial distribution of the preservative should be determined in-situ, without disturbing the normal wood structure. Direct-scan X-rays represent one potential method for determining chemical levels in a solid wood specimen.

Direct-scan X-ray densitometry has been increasingly used to determine density values in plantation-grown wood species; it has the capability to measure average density values (i.e., ring density or average sample density) to within a standard deviation of ±0.011 g/cm^3.[3] This report describes how well direct-scan X-raying predicts retention and distribution of chromated copper arsenate in the sapwood of a conifer.

MATERIAL AND METHODS

Clear, flat-grained wafers (0.33 cm thick by 5 cm wide by 7.63 cm long) were cut from the tangential faces of 13 western

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hemlock (Tsuga heterophylla (Rod) Sarg.) boards. All wafers were then conditioned to approximately 6% moisture content. From each of the 13 boards, 7 wafers were each randomly assigned to a different one of 7 treatment groups, so that the statistical design was a random block. The 13 wafers in one of the groups were untreated and served as controls. Each of the other 6 groups of 13 wafers was pressure-treated with a solution of chromated copper arsenate (Type C) at a different concentration: 0.5, 1.0, 1.5, 2.0, 2.5, or 3.0%, on an oxide basis. The pressure-vacuum treatment consisted of an 880-mb (26-inch) vacuum drawn for one-half hour and followed by a 4-hour pressure applied at 880 kPa (125 psi). Several additional wafers were included in each of the 7 groups to serve as extras, as needed. The treated wafers were air-dried to constant weight at 21°C (70°F) and 58% relative humidity to permit chemical fixation and then oven-dried to eliminate moisture.

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Direct-Scan X-ray System

A direct-scan X-ray system[3] was used to measure the intensity of X-rays passed through the wafers in the different treatment groups. The scanning system consisted of an X-ray tube, a high-voltage power supply, a lead-lined containment box, a scanning tray that moved a specimen beneath the stationary X-ray tube, a Victoreen photodiode X-ray scintillation detector with an output current to a Victoreen picoammeter, and a desk-top computer for equipment control, data acquisition, and data analysis.

For each scan, a Delrin® acetal wedge was used to verify system stability. It was fastened to the scanning tray 10 mm from the end, thereby creating an air-gap of 10 mm in the scan. (X-rays pass unrestricted through air and at a consistent,

restricted rate through Delrin®; consequently, the ratio of X-ray intensity through these two mediums should be constant as long as the X-ray's energy spectrum remains the same.) The wood wafer was placed on the tray immediately after the Delrin® wedge, and the containment box was closed. A stepper motor moved the scanning tray in 0.1007-mm steps (4 steps/sec). At each step, X-rays were passed through the air-gap, the Delrin® wedge, or the wood wafer and then through an aperture mounted on the scintillation detector. The scintillation detector generated a current proportional to the amount of X-radiation passing through the material. (High-density wood--including that impregnated with chemicals--will absorb more X-rays than low-density wood and produce a correspondingly lower X-ray intensity as measured by the detector current.) The detector current was converted to voltage by a picoammeter. Voltage was sampled by a 12-bit analog-to-digital converter board in a desk-top computer that collected and stored the digital data. The digital representation of a picoammeter voltage will henceforth be referred to in this paper as X-ray intensity. (X-ray intensity can be converted back to picoammeter-volts by dividing by 4095 and multiplying by 10 volts.)

The process was continued until the full 110-mm scan length was traversed. Initially, the aperture of the X-ray sensor was 1.4 mm in diameter, but it was later replaced by one measuring 0.1 mm by 1 mm. The X-ray was excited at 25.3 kV; tube current was 1 mA. Each scan consisted of 1100 steps, with 20 readings averaged per step to reduce noise. A scan required 4.6 minutes to complete, not counting time to return the scanning tray and transfer data to a floppy disk for analysis.

X-ray intensity dropped over time, perhaps because of heating of the sensor. The drop was evident when X-ray intensity through air was compared at the beginning and end of each scan.

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This drop, however, did not alter the absorption characteristics of the X-ray spectrum[3]. The Delrin® wedge and wood wafer will absorb a constant percentage of X-rays regardless of their intensity. If the intensity drop is large, however, it must be compensated for so that the mean X-ray intensity through the wafer can be accurately computed. Therefore, a linear correction over time was applied to the intensity data in each scan. Next, in order to make scans comparable with each other, the X-ray intensity data in each scan were adjusted by the following formula:

$$y_i = x_i \cdot (4000/A_0) \qquad [1]$$

where

i = 1 to 1100
y_i = adjusted X-ray intensity at step i
x_i = unadjusted X-ray intensity at step i
A_0 = average X-ray intensity through air

A random-block analysis[4] was made of the mean X-ray intensity generated by scans through each wafer in the seven treatment groups. This analysis determined if the statistical blocking by boards removed a source of variation from experimental error, thus increasing the precision of the estimates of treatment means as compared to that with completely randomized design; it also determined if there were significant differences among treatment means.

X-ray Fluorescence Analysis

After the X-ray scanning, the wafers were ground and analyzed for CCA retention by X-ray fluorescence. First, a 1.59-cm strip was cut from the wood surrounding the site of the

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X-ray scan of each wafer assigned to the random-block design. One of the extra wafers from each treatment group was cut across its width into three sections so that preservative retention levels could be compared within wafers as well as among wafers. The middle section was 3 cm long, and the two end sections were each 2 cm long. Each section was ground for 30 seconds in a coffee grinder. From each grinding, 1 g of material was poured into a small pan (provided by ASOMA Instrument), compacted by applying a torque of 25 N•m with a hand press, and placed in an ASOMA-8620 X-ray fluorescence analyzer. Preservative retention was expressed as kg/m^3 on the basis of oven-dry volume and weight of each wafer.

The mean X-ray intensities generated by scans through each wafer in the seven treatment groups were regressed on preservative retention by the wafers as measured by the ASOMA-8620 X-ray fluorescence analyzer in order to determine how accurately direct-scan X-raying measured preservative retention.

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Variability of X-ray Scans Over Time

Repeatability of scans over time was determined from randomly selected scans through air and Delrin® at intervals up to 9 months; scans through the two media were compared in terms of the means, ratios of the means, standard deviations, and coefficients of variation of X-ray intensity. Because air and Delrin® are homogeneous materials, repeated scans did not have to cover exactly the same path in order to be comparable. The same equipment was used for all scans except that the original 1.4-mm-diameter lead aperture of the X-ray sensor was replaced in January 1989 by a brass aperture 0.1 mm wide by 1 mm long. Because of the smaller aperture, current to the X-ray tube was increased from 1 mA to 2 mA. The smaller aperture was

substituted because decreasing aperture size increases system resolution, since X-rays are passed through a relatively smaller portion of wood at each scan step. If direct-scan X-rays were to be used to measure spatial distribution of preservative in a small volume of wood, such as around tooth incisions, system resolution would become an important factor. It has been stated that decreasing aperture size increases system variability[3].

In some scans, the step increment was reduced from 0.1 mm per step to 0.05 mm per step in order to increase system resolution. X-ray intensities were then compared in order to determine if decreased step increment affects system variability.

X-ray intensities were not linearly corrected for drop during each scan because the drop was slight, usually only one or two intensity points. X-ray intensities for each scan were, however, adjusted so that the means of all scans could be compared (Eq. 1).

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Variability of X-ray Intensity at a Single Scan-Step

If direct-scan X-rays were to be used to measure spatial distribution of preservative in a small volume of wood, accurate measurements of preservative retention at a single site would be especially important. Variation of X-ray intensity during a single scan-step was determined by positioning the X-ray head over a randomly selected site on one wafer in each of the seven treatment groups, as well as over Delrin® and over air. While the scanning tray was held stationary, 1000 readings of X-ray intensity were collected per scan and the mean, standard deviation, and coefficient of variation were computed. Because X-ray drop during each scan was negligible, no adjustments were made for it. Nor were X-ray intensities for each scan adjusted according to equation 1; this adjustment was omitted because data on X-ray intensity through air was not collected for every scan.

In addition, one untreated wafer and one wafer treated with 3% preservative were scanned twice. The scanning tray was returned between the first and second scan without moving the wafer, thus ensuring that X-rays were passed through the same sites in consecutive scans.

RESULTS

X-ray Scans

Intensities of X-rays passed through a wafer treated with preservative containing 3% oxide are shown in Fig. 1. Intensities of 4000 at the beginning and end of the scans represent unrestricted X-ray passage through air. Intensities of approximately 2800 after the initial air readings represent X-ray passage through the Delrin® wedge. X-ray passage through the wood wafers was inversely proportional to preservative concentration (higher oxide concentrations were associated with decreased X-ray intensity). Intensities were lower at the ends of the treated wafers than in the mid-sections, probably because of more easily treated end grain. The nearly vertical lines connecting intensities through air, Delrin®, and wood wafers in Fig. 1 result from the small advances made by the scanning tray (0.1007 mm/step); individual steps occasionally caused varying proportions of the different materials to be scanned simultaneously. Even though the wood wafer was positioned against the Delrin®, there was a small air space separating them; this space caused the intensity peak between Delrin® and wafer.

The analysis of variance (Table 1) showed that there were significant differences between treatment means. Blocking by board effectively increased the precision of this experiment. The relative efficiency of the randomized block design compared to a

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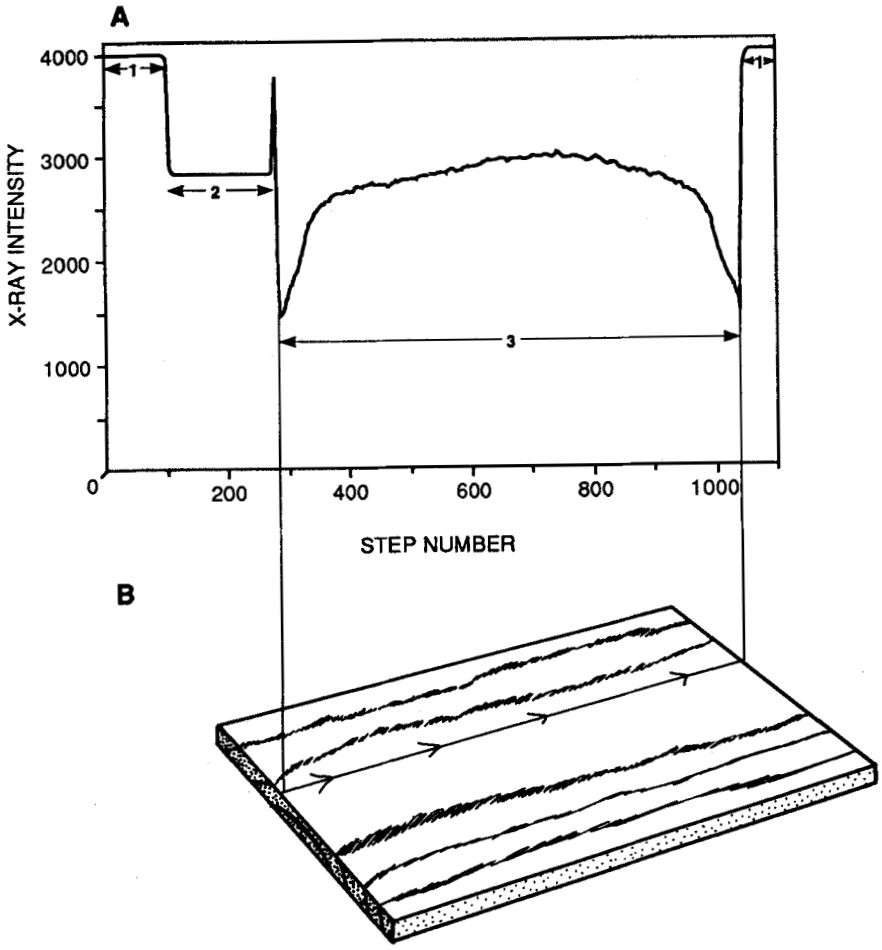

FIGURE 1. (A) Intensity of direct-scan X-rays passed through (1) air, (2) Delrin® wedge, and (3) wood wafer treated with CCA type C preservative solution. (B) Tangential and radial faces of western hemlock wafer (0.33 cm thick by 5 cm wide by 7.63 cm long), showing X-ray scan path.

TABLE 1

Analysis of Variance of Intensity of Direct-Scan X-rays Passed Through Preservative-Treated Wood Wafers in a Random-Block Design

Source of variation	Sum of squares	d.f.	Mean square	F-ratio	Sig. level
Preservative treatment	8895670.7	6	1482611.8	558.947	<0.0001
Board	184222.2	12	15351.9	5.788	<0.0001
Error	190980.68	72	2652.5095		
Total	9270873.7	90			

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completely randomized design was 1.64; therefore, blocking by board increased the efficiency by 64%. If a completely randomized design had been used, 22 replications per treatment group would have been required to attain the same precision as was provided by the 13 replications (boards) of the randomized block design.

Mean separation based on Newman-Keuls' method (Table 2) showed that X-ray intensities for the various treatment groups differed significantly, with one exception: intensities for wafers treated with 2% preservative were not significantly different from those for wafers treated with 1.5% preservative.

Preservative Retention

Mean separation based on Newman-Keuls' method showed that preservative retentions by the wafers in each of the seven treatment groups were indeed significantly different from each other (Table 2). Although mean separation of X-ray intensities

TABLE 2

Intensities of Direct-Scan X-rays Passed Through Preservative-Treated Wood Wafers and Preservative Retention by Those Wafers

Concentration of CCA in treatment solution (% oxide)	No. of wafers	Mean X-ray intensity*1	Preservative retention*1,*2 (kg/m³)
0	13	3629 a	0.134 a
0.5	13	3458 b	5.552 b
1.0	13	3340 c	9.922 c
1.5	13	3135 d	16.563 d
2.0	13	3106 de	18.618 e
2.5	13	2820 f	27.723 f
3.0	13	2686 g	32.539 g

*1 Values followed by the same letter(s) are not significantly different from each other according to Newman-Keuls' mean separation procedures at $\alpha = 0.05$.

*2 Measured by the ASOMA-8620 X-ray fluorescence analyzer.

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for the same wafers indicated that preservative retentions in wafers treated with 2% concentration were not significantly different from those in wafers treated with 1.5% concentration, the difference between mean retentions of these two groups was small when compared to those between mean retentions of the other groups.

Regardless of concentration, preservative retention as revealed by X-ray fluorescence analysis was greater at the ends of wafers than in their mid-sections (Table 3). These data indicate that intensities were lower after X-rays had passed through the ends than through the mid-sections of treated wafers because preservative retentions were higher in the ends. When average intensities of X-rays passed through these sections were regressed on the corresponding preservative retentions as

TABLE 3

X-ray Fluorescence Analysis of Six Wafers Treated with CCA Type-C Preservative Solutions

Concentration of CCA in treatment solution (% oxide)	Preservative retention (kg/m^3) in--		
	2 cm on left end of wafer	3 cm in mid-section of wafer	2 cm on right end of wafer
0.5	8.3	4.4	10.4
1.0	18.1	7.8	15.1
1.5	22.7	12.7	25.0
2.0	30.3	16.0	23.2
2.5	37.9	23.2	38.8
3.0	42.9	33.8	38.4

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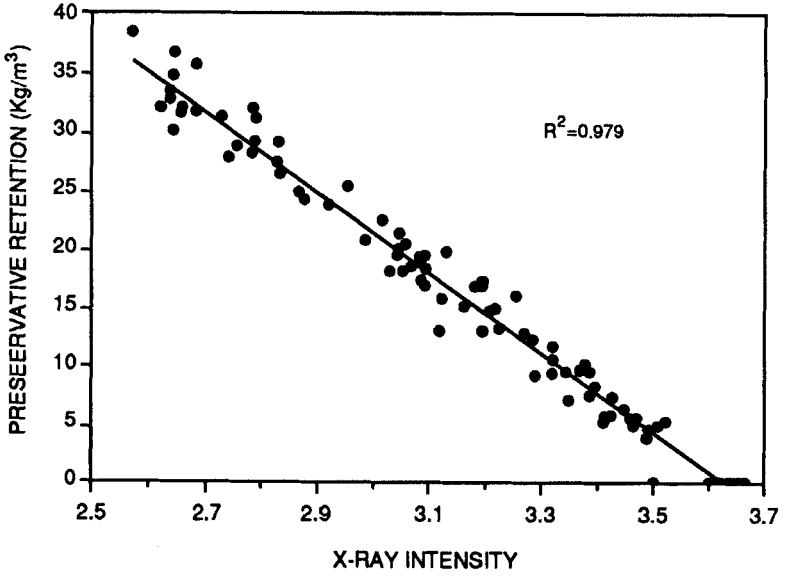

FIGURE 2. Regression of average intensity of direct-scan X-rays passed through preservative-treated wafers on corresponding preservative retention of a 1.59-cm strip surrounding the scan site as revealed by X-ray fluorescence analysis.

indicated by X-ray fluorescence analysis, X-ray intensities were found to predict 95% of the variation in preservative retention. And when average intensities of X-rays passed through every wafer in the random-block design were regressed on the corresponding preservative retention by a 1.59-cm strip surrounding the site of the X-ray scan, X-ray intensities were found to predict 98% of the variation in preservative retention among wafers (Fig. 2). The prediction equation was $Y = 124.237 - 0.0342\ x$ and the standard error of the prediction was 1.6 kg/m^3.

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Variability of X-ray Scans Over Time

Intensities of X-ray scans through air and Delrin® at intervals up to 9 months were consistent as long as the aperture on the scintillation detector remained the same (Table 4). Different apertures produced different air-to-Delrin® intensity ratios. This change probably occurred because the two apertures made of different metals had different effects on the X-rays collected by the photodiode scintillation detector. The differing ratios mean that X-rays collected by different apertures are not comparable unless intensities are adjusted.

Decreasing aperture size, which increases system resolution, approximately doubled variation in X-ray intensity, probably because a smaller portion of the scintillation detector was being excited. With the larger, 1.4-mm-diameter aperture, X-ray intensities had a coefficient of variation (CV) of 0.04% to 0.07% of the mean, while the smaller, 1- by 0.1-mm aperture resulted in a CV of 0.1%.

Decreasing the scan-step size, which increases system resolution, had no effect on system stability or system variability.

TABLE 4

Intensities of X-rays Passed Through Air and Delrin® at Intervals up to 9 Months When Two Sizes of Apertures and of Scan Steps Were Used*1

Date	Aperture*2 (mm)	Air $\bar{Y}$	Air s	Air CV (%)	Delrin® $\bar{Y}$	Delrin® s	Delrin® CV (%)	Air / Delrin® (intensity ratio)
Nov 1 '88	1.4 diam.	4000	1.68	0.04	2798	2.01	0.07	1.429
Nov 2 '88	1.4 diam.	4000	1.42	0.04	2798	2.00	0.07	1.429
Jan 12 '89	1 x 0.1	3998	3.45	0.09	2821	3.25	0.11	1.417
Jan 12 '89	1 x 0.1	4003	3.97	0.10	2826	3.14	0.11	1.416
Jan 12 '89	1 x 0.1	4000	3.86	0.10	2824	3.55	0.13	1.416
Mar 16 '89	1 x 0.1	3999	3.78	0.09	2822	3.43	0.12	1.417
Apr 26 '89	1 x 0.1	4000	3.95	0.10	2823	3.36	0.12	1.417
Apr 26 '89	1 x 0.1	4002	3.65	0.09	2820	3.63	0.13	1.419
May 11 '89	1 x 0.1	4000	3.53	0.09	2820	3.25	0.11	1.418
June 6 '89	1 x 0.1	4000	3.50	0.09	2819	3.76	0.13	1.419

*1 $\bar{Y}$ = mean intensity.
s = standard deviation.
CV (coefficient of variation) = $s/\bar{Y} \times 100\%$.

*2 Scan steps were 0.1 mm for the first seven scans and 0.05 mm for the last three scans.

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Variability of X-ray Intensity at a Single Scan-Step

One thousand readings of X-ray intensity at a single scan-step had a CV of 0.1% when X-rays were passed through air, Delrin®, untreated wood wafers, or wood wafers treated with any of the six CCA preservative solutions (Table 5). The small variation in intensity readings indicates that direct-scan X-ray techniques could provide a detailed representation of chemical distribution within a wood specimen.

TABLE 5

Variability of X-ray Intensity During 1000 Readings at a Single Scan-Step*1

Material scanned	$\bar{Y}$	s	CV (%)
Air	3990	3.89	0.10
Delrin®	2807	3.42	0.12
Untreated wood wafer	3643	3.63	0.10
Treated wood wafers (% oxide)*2			
0.5	3539	3.64	0.10
1.0	3438	3.58	0.10
1.5	3302	3.60	0.11
2.0	3331	3.52	0.11
2.5	3188	3.55	0.11
3.0	3162	3.49	0.11

*1 $\bar{Y}$ = mean intensity. X-ray intensities were not adjusted by equation [1].
s = standard deviation.
CV (coefficient of variation) = $s/\bar{Y} \times 100\%$.

*2 Concentration of CCA in treatment solution.

Plots of two consecutive full-length scans through air, Delrin®, and a wood wafer treated with 3% preservative and of two consecutive scans through air, Delrin®, and an untreated wood wafer illustrate the slight variation in X-ray intensity at single scan-steps in repeated scans (Fig. 3). Comparisons of the two sets of X-ray scans indicated that both displayed variations in intensity attributable to background noise; however, the scans through treated wood displayed additional variation because of corresponding variation in preservative concentration in wood cells.

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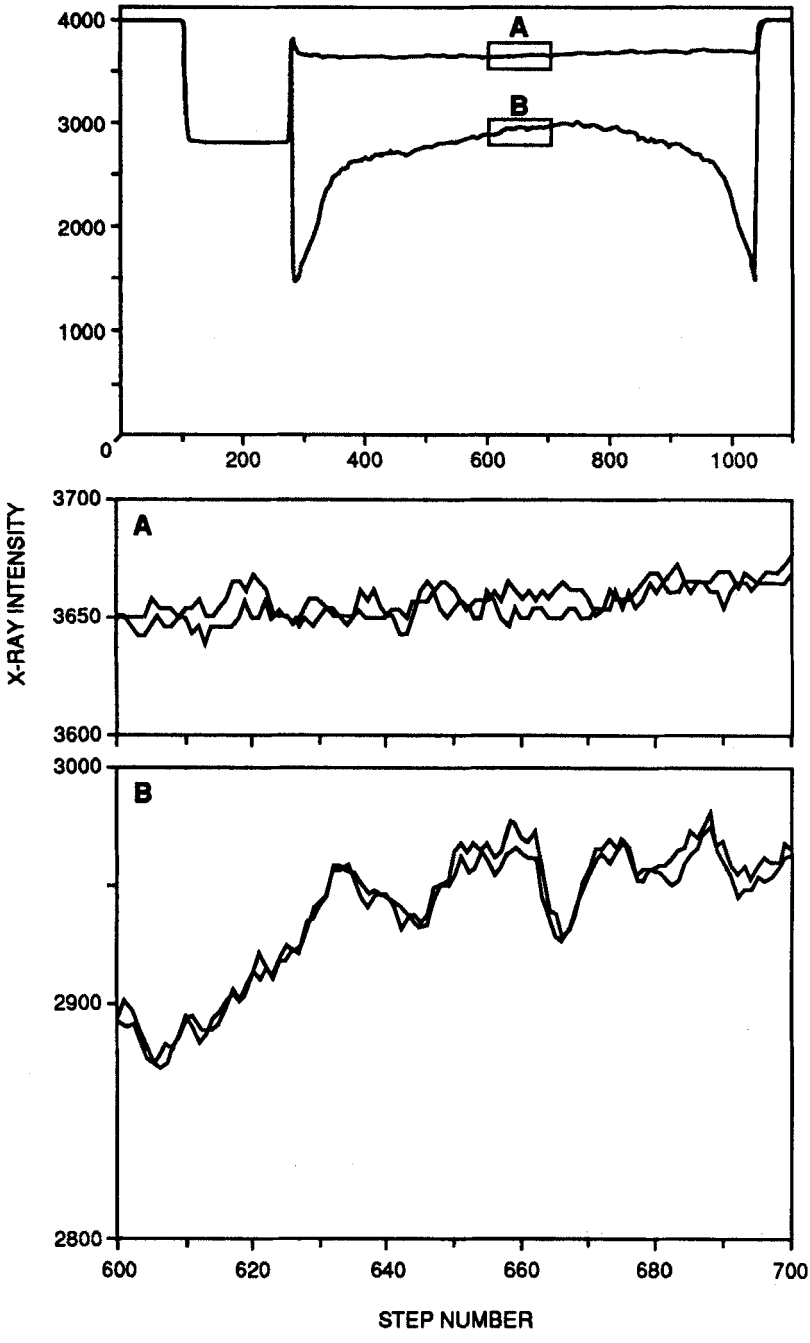

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CONCLUSIONS

The results indicate that direct X-ray scanning of wood treated with inorganic arsenicals can provide a non-destructive way to assess gross preservative content. However, the technique presupposes that untreated material of similar density is available for comparison. Scanning can be used to assess distribution of preservative in wood without destroying the wood matrix; it provides a more detailed image of chemical distribution than would be possible by conventional grinding and chemical analysis. While not practical for routine analysis, this technique holds promise for assessing preservative distribution in relation to wood characteristics such as heartwood/sapwood interfaces, latewood/earlywood differences, or tooth incisions.

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FIGURE 3. Plots of (A) two consecutive scans through air, Delrin®, and an untreated wood wafer and (B) two consecutive scans through air, Delrin®, and wood wafer treated with 3% oxide CCA preservative. Enlargements of indicated plot segments (boxed) appear beneath the plots.

REFERENCES

1. J.T. Micklewright, Proc., Am. Wood-Preserv. Assoc. 84, 343 (1988).
2. Book of Standards, American Wood-Preservers' Association, Stevensville, Maryland, 1988.
3. M.L. Hoag, Measurement of within tree density variations in Douglas-fir (Pseudotsuga menziesii (Mirb.) Franco) using direct scanning x-ray techniques. M.S. thesis, Oregon State University, Corvallis, 1988.
4. R.G.D. Steel and J.H. Torrie, Principles and Procedures of Statistics: A Biometrical Approach, p. 195-215, McGraw-Hill, New York, 1980.

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